

Electric Field Induced Phase Transition in KDP Crystal Near Curie Point: Raman and X-ray Scattering Studies

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Abstract

X-ray scattering measurements are performed in order to verify that the mechanism leading to the DC electric field induced $C_{2v}^{19} \rightarrow C_{2v}^{\neq 19}$ phase transition in KDP crystal at 119 K is the changing of the local sites symmetries of phosphate group from C_2 in the C_{2v}^{19} phase to C_s in the $C_{2v}^{\neq 19}$ phase. It is shown by analyzing the integrated intensity of the (800) and (080) reflections that under DC electric field the density of oxygen atoms lying on these plane changes indicating that phosphate group rotates around the [010] direction relative to the orthorhombic C_{2v}^{19} structure. Some Raman results are also discussed.

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Among the several ferroelectric materials which contains hydrogen bonds, potassium dihydrogen phosphate (KDP) is probably the most investigated. At a temperature of 122 K, the KDP crystals undergo a ferroelectric phase transition, where occurs the lowering of the crystal symmetry from the tetragonal D_{2d}^{12} phase to the orthorhombic C_{2v}^{19} phase. As a result the crystal lattice becomes polarized along the $c - axis$. Near and below the phase-transition temperature the protons are partially ordered [1], being located near either the upper or the lower oxygen atoms of phosphate groups. Many works reporting on the investigation of the stability of both D_{2d}^{12} and C_{2v}^{19} phases as a function of the hydrostatic pressure and low-intensity DC electric fields were already published [2-7]. Recently, we have investigated the effect of uniaxial pressure on these KDP phases [8]. We have shown that under uniaxial pressure, where the force was applied along the shear direction, the KDP undergoes two metastable transitions, namely: (i) $D_{2d}^{12} \rightarrow C_{2v}^{j \neq 19}$ and (ii) $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$. A reasonable explanation for these transitions was given based on the changing of the local site symmetry of the phosphate ions. In the ferroelectric phase, the phosphate ion changes its local site symmetry from C_2 to C_s , maintaining the same factor group C_{2v} but modifying the space group. These changes are due to the rotation of the phosphate ions around the [010] direction of the orthorhombic structure. (It is important to mention that under an electric field and low temperature a phase transition from a monoclinic C_s structure to an orthorhombic C_{2v} one was observed [9]). Also, after discussing the reversibility criteria of this new metastable phase, we have drawn the phase diagram for the KDP transitions on the plane (σ_6, T) for temperatures in the range from 110 K to 130 K. A theoretical explanation to the appearance of the metastable $C_{2v}^{j \neq 19}$ phase based on the Gibbs free energy density of the system was given. We have expanded the phenomenological Gibbs free energy density of system up to P_3^{10} , where P_3 is the spontaneous polarization along the [001] direction. Even for small values of the coefficient of the term P_3^{10} , a second minimum for the crystal energy can be achieved. This second minimum is associated to the metastable $C_{2v}^{j \neq 19}$ phase, which presents a lower value of polarization than that presented by the stable C_{2v}^{19} phase. This is in accordance with our assumption that the dipoles rotate around the orthorhombic

$b - axis$ when KDP undergoes a phase transition. This assumption can also be verified using other experimental techniques, e.g., X-ray diffraction, where we can observe modifications in the diffraction pattern associated with the $(h00)$ and $(0k0)$ reflection planes, with $h, k = 4n$ where $n = 1, 2, \dots$, once the number of oxygen atoms lying on these planes change. However, it is somewhat difficult to perform X-ray scattering measurements using the stress apparatus described in Ref.[8]. So, we decided take advantage of the fact that the ferroelectric phase present piezoelectricity, to investigate the phase transition $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$ under DC electric field applied along the $[001]$ ferroelectric direction. In other words, due to the converse piezoelectric effect a DC electric field applied along the $[001]$ direction should induce phase transitions in KDP crystals similarly to that induced by uniaxial pressure with the force applied along the shear direction. Hence, the main goal of this work is to perform x-ray diffraction measurements to verify the assumption that due to a DC electric field applied along the ferroelectric $c - axis$, the dipoles rotate around the $[010]$ direction of the orthorhombic structure leading to a change in the local site symmetry of the phosphate ions.

The samples were cut from good optical quality crystals grown by slow evaporation in parallelepipeds of dimensions $6 \times 5 \times 1.5 \text{ mm}^3$ and oriented by X-ray diffraction . The parallelepipeds faces were orthogonal to the $[100]$, $[010]$ and $[001]$ directions to the orthorhombic structure. Electrodes of silver were evaporated on the large faces which are perpendicular to the ferroelectric $[001]$ direction. A Keithley Instruments voltage supply model 246 was used as the voltage source.

Light scattering measurements were performed using a conventional equipment (argon ion laser and double monochromator), with an experimental resolution of 1 cm^{-1} . A continuous flow-type cryostat was used to record the Raman spectra at low temperatures, which could be controlled to $\pm 0.1 \text{ K}$. Geometries for the spectra listed in the figures follow the usual Porto notation A(BC)D. X-ray scattering measurements were performed using a Rigaku diffractometer with radiation source of Mo $K\alpha$ coupled with a low temperature chamber. The good penetration of X-ray beam gives advantage to get diffraction from deeper planes, avoiding the non uniformity of electric field on surface. The procedure used in the X-ray ex-

periments was: first, the crystal was aligned using the (440) reflection of paraelectric phase and then cooled down to ferroelectric phase where during the transition, the reciprocal lattice points of (800) and (080) reflections appear satisfying the diffraction conditions of the orthorhombic structure with the C_{2v} factor group.

Before discussing X-ray results, we need to show that under DC electric field, KDP crystal undergoes the $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$ phase transition. Then, in Fig. 1(a) and 1(b) we show part of DC electric field dependent Raman spectra for the low frequency taken at 119 K, for the symmetries A_1 and B_1 of the C_{2v} factor group, respectively. For $E = 0$, both A_1 and B_1 spectra present a good agreement with the mode distribution predicted by the group theory analysis. However, for $E = 5$ kV/cm, we observe qualitative modifications in the Raman spectra. From Fig. 1(a) we can see three modifications: (i) The increase of the vibration for $\omega < 250$ cm⁻¹; (ii) the increase in the intensity of the vibration at 525 cm⁻¹ and (iii) the disappearance of the vibration at 575 cm⁻¹. For B_1 symmetry, as shown in Fig. 1(b), we observe an inversion in the intensity of the peaks oscillating at around 200 and 500 cm⁻¹. Since the symmetries A_1 and B_1 are unidimensional, the modifications exhibit by the Raman spectra are an evidence that due to the DC electric field the C_{2v}^{19} phase of KDP underwent a phase transition. The modifications observed comply with the symmetry analysis considering the transition from the space group C_{2v}^{19} to the space group $C_{2v}^{j \neq 19}$, where the phosphate ion changes its local site symmetry from C_2 to C_s . The modifications observed are irreversible once all features seen in the Raman spectra of Figs. 1(a) and 1(b) remain present even when the DC electric field is turned off, and the crystal is maintained in this condition for an arbitrary long time. To go back to the spectra of KDP for the C_{2v}^{19} phase, we must increase the temperature of the crystal over 122 K, and then cool it again at temperatures below 122 K. This irreversibility can be understood as a manifestation of a lowering in the cell potential due to an increase in the dipole interactions. Switching off the DC electric field is not sufficient to overcome the potential barrier created by dipolar interaction. This barrier is overcome only by transferring thermal energy to the dipoles. Due to these facts, we conclude that a DC electric field induces a phase transition in KDP

similar to that induced by uniaxial pressure.

In order to present another experimental evidence of the mechanism leading to the appearance of the $C_{2v}^{j \neq 19}$ phase, we have performed single crystal X-ray measurements as a function of DC electric field. The idea of the experiment is very simple: if the phosphate tetrahedron in fact rotates around the $[010]$ direction, a variation in the behavior of the integrated intensity of diffraction peaks associated with (800) and (080) reflection planes should be observed, once the number of oxygen lying on these planes changes when E is varied from 0 up to 5 kV/cm, as shown in Fig. 2. Figure 3 shows the diffraction patterns corresponding to the (800) and (080) reflection planes of the orthorhombic structure as a function of the DC electric field up to 5 kV/cm at 119 K. The features observed are irreversible in the same way that those presented in the Raman spectra. The peaks emerge from overlapping of the bands corresponding to the $K\alpha_1$ and $K\alpha_2$ lines of Mo radiation. By performing a spectral decomposition into pseudo-Voigth components, we can draw the behavior of the integrated intensity of the (800) and (080) $K\alpha_1$ reflections as a function of DC electric field as displayed in Fig.4. It should be observed that the integrated intensity corresponding to (800) reflection decreases with increasing the DC electric field up to 5 kV/cm, while that one of (080) reflection increases. These changes in the integrated intensity behavior indicate that the density of oxygen atoms lying on these planes changed. This can be ascribed as a result of a rotation of phosphate ion around the $[010]$ direction relative to the C_{2v}^{19} orthorhombic structure. This statement agrees with the observation performed by Bacon and Pease [10], where they showed that the KDP under DC electric field exhibits the value of the saturation polarization of the order of 4.7×10^{-6} Ccm $^{-2}$, whereas the observed value is 5×10^{-6} Ccm $^{-2}$ for $E = 0$ [11]. Due to this fact, the local sites symmetries exhibited by the phosphate ion changes from C_2 to C_s which modifies the space group of the C_{2v} symmetry from $j = 19$ to $j \neq 19$. In conclusion we reported on the experimental verification based on X-ray measurements of the mechanism leading to the conformational $C_{2v}^{19} \rightarrow C_{2v}^{j \neq 19}$ phase transition of KDP when a DC electric field is applied along the ferroelectric c axis. The behavior of the integrated intensity of (800) and (080) reflections indicates that occurs a modification in the

density of oxygen atoms lying on these planes . This modification results from the rotation of phosphate ion around the orthorhombic [010] axis. This rotation changes the local sites symmetries of phosphate ion from C_2 in the C_{2v}^{19} phase to C_s in the $C_{2v}^{\neq 19}$ phase.

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FIGURE CAPTIONS

Fig. 1- Raman spectra of KDP as a function of the DC electric field at 119 K for two different symmetries: (a) A_1 and (b) B_1 .

Fig. 2- Schematic representation of the orthorhombic C_{2v}^{19} structure of the KDP projected on the ab plane.

Fig. 3- Experimental single crystal X-ray diffraction pattern related to (800) and (080) reflection planes as a function of the DC electric field at 119 K.

Fig. 4- Plots of the integrated peak intensity corresponding to (800) and (080) $K\alpha_1$ reflections as a function of the DC electric field at 119 K.

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